

**MODELS FOR ASSESSING THE VOLATILIZATION
OF HERBICIDES APPLIED TO FLOODED RICE FIELDS**

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ABSTRACT

Volatilization rates of MCPA, thiobencarb, and molinate from water were calculated using the EXAMS aquatic fate computer model, and measured in a laboratory chamber and in flooded rice fields. A fair to good correlation was obtained between EXAMS-calculated and chamber-measured rates for all three herbicides. Field-measured values correlated well with chamber-measured rates for thiobencarb and molinate. For MCPA, field-measured values were much higher than expected for volatilization from water alone. In this case, the presence of plant and other surface residues in the field made the major contribution to observed volatilization. For MCPA, 4-chloro-o-cresol flux was comparable to that of the parent herbicide.

INTRODUCTION

The atmospheric movement of pesticide residues from treated to non-target areas may lead to unintentional exposures for humans, animals, and plants in the vicinity of sprayed fields. Residues may enter the air as drift during application or by post-application volatilization (1-3). Some variables which affect the rate of entry to the air are amenable to mathematical modeling and laboratory simulation, but only a few field measurements have been made for specific chemical-crop combinations to assist in model design and validation (4).

A potentially important drift-volatilization situation stems from the use of herbicides in flooded rice culture in the Sacramento Valley of California, where MCPA, thiobencarb, and molinate are among the chemicals used extensively to control broadleaf and graminaceous weeds. These herbicides are applied in a relatively short interval, primarily in May and June, in areas frequently close to orchards and residences. Potential orchard damage from MCPA drift, and potential human illness from inhaling molinate vapors, are among the concerns associated with airborne residues of these herbicides.

We have assessed the rate of volatilization of these three chemicals from water using three techniques: (1) Computer model prediction using the EXAMS aquatic fate model; (2) laboratory chamber measurement; and (3) field measurement of volatilization flux over commercial rice paddies. Our goal was to evaluate EXAMS and the laboratory chamber as tools for predicting volatilization losses from flooded fields.

MATERIALS AND METHODS

Chemicals and Solvents

Standards of MCPA (2-methyl-4-chlorophenoxyacetic acid), MCPA-DMA (MCPA-dimethylamine salt), and CLOC (4-chloro-o-cresol) were obtained from the Dow Chemical Co. Standards of thiobencarb [S-(4-chlorobenzyl)N,N-diethylthiolcarbamate] and molinate (S-ethyl hexahydro-1H-azepine-1-carbothioate) were obtained from the U.S. Environmental Protection Agency. The MCPA formulations used were principally MCPAmine (Dow, 0.48 kg a.i./L), Rhomene (Rhodia, 0.48 kg a.i./L) and MCPA-DMA (Platte, 0.48 kg a.i./L). The thiobencarb formulation was Bolero 10 G (Chevron, 10% a.i. granular) while the molinate formulation was Ordram 10 G (Stauffer, 10% a.i. granular). XAD-4 macroreticular resin (20/50 mesh, Rohm and Haas) was prepared by washing with water followed by acetone, and Soxhlet extractions with methanol followed by diethyl ether for 24 hr each. The cleaned resin was dried at 50°C in a vacuum oven overnight. XAD-2 resin (20/50 mesh, Rohm and Haas) was prepared in a similar manner, except for the use of dilute hydrochloric acid prior to water in the initial washing step. Florisil (60/100 mesh, PR grade, Floridin Co.) was activated at 110°C overnight in a drying oven before use. All organic solvents were Nanograde[®] (Mallinckrodt) or equivalent. Diazomethane (CAUTION: EXPLOSION HAZARD) was prepared from N-methyl-N-nitroso-p-toluenesulfonamide (Aldrich) and employed in diethyl ether solution.

Gas Chromatography (GC)

GC for methylated MCPA and CLOC was done on a Dohrmann or Microtek MT 220 gas chromatograph equipped with a Dohrmann Model C-200 microcoulometer, a Model P-100 furnace control, and a 1.5 m x 6 mm (OD) glass column packed with 10% DC-200 on 80/100 mesh Gas Chrom Q at 150°C, or an equivalent column. Gas flows were 18, 50, and 80 mL/min for carrier (N₂), make-up (N₂), and reaction (O₂) gases, respectively. Confirmation of MCPA and CLOC in some of the air samples (four out of over 100) was accomplished using a Finnigan Model 3200 gas chromatograph/mass spectrometer (GC/MS) equipped with a Model 6000 data system and a 30 m glass capillary column coated with SP 2250 (Supelco) which was programmed from 100 to 240° at 8°/min.

GC for thiobencarb and molinate field air and water samples was done on a Varian Model 3700 gas chromatograph equipped with a TSD detector and a 30 m SE-54 capillary column operated at a split ratio of 100:1. The oven temperature was programmed from 100° (2 min initial hold) to 270° (water) or 240° (air) at 10°/min. Injector and detector temperatures were both 250°. (These analyses were performed by the California Department of Food and Agriculture, Environmental Monitoring Section, Chemistry Laboratory Services, Sacramento, CA). GC for thiobencarb and molinate laboratory chamber samples was done using a Microtek MT 220 gas chromatograph equipped with an FPD detector (sulfur mode) and a 1.5 m x 6 mm (OD) glass column packed with 3% OV 210 on 80/100 mesh Chromosorb W HP. The oven temperature was 120° and the detector was 180°; and the injector temperature was 225°. The carrier gas (N₂) had a flow of 70 mL/min and the detector gas flows were 5 (O₂), 60 (H₂) and 100 mL/min (air).

EXAMS Calculations

The IBM 50-compartment version of EXAMS was provided by the U.S. EPA, Environmental Research Laboratory (Athens, GA), and adapted to a Burroughs 6800 computer system. The use of EXAMS was according to the general directions in Burns et al (5) while the specific use for this study was as described previously (6, 7). EXAMS requires as a minimum environment at least one littoral and one benthic compartment. A very small benthic compartment (1×10^{-8} m depth) was used so that this compartment and its input parameters had a negligible effect on the calculated rates.

Transfer rates between soil and water were assumed to be rapid relative to volatilization rates, and were set as recommended in the EXAMS manual (5). For the herbicides used in this study the appropriate physicochemical properties were entered, and the volume (310 ml) and depth (4.1 cm) of the compartments as well as the wind speed (1.0 m/sec), pH (8.5), and temperature (22°) were made equal to those of the laboratory chamber. Pesticide loads (inputs) were entered (in kg/hr) using DRFLD(1), a miscellaneous loading into water. The maximum loads allowed by EXAMS into the water system were as follows (kg/hr): MCPA, 1.0×10^{-12} , thiobencarb, 1.0×10^{-12} , and molinate, 6.18×10^{-9} . In all cases, the steady state concentrations achieved with these loads were below the initial concentrations present in the laboratory experiments. However, this did not affect the value of the first order rate constants needed for calculations. Flux values (in $\text{ng}/\text{cm}^2 \cdot \text{hr} \cdot \text{ppm}$) were calculated by multiplying the first order volatilization rate constant (in hr^{-1}), obtained from the half life for volatilization as output by EXAMS, by the water depth (in cm) and by 1000.

Laboratory Volatilization

Volatilization from water was studied in the chamber described previously (6, 8). A 14.4 cm diameter glass crystallizing dish was filled to the brim with a water solution of either MCPA (initial concentration 95 mg/L), thiobencarb (16.3 mg/L), or molinate (25.1 mg/L). For MCPA, the initial pH was adjusted to 3.5 with HCl. Humidified air (85% relative humidity) was passed over the water surface at a flow rate of 20 L/min, corresponding to a wind velocity of 2.2 m/sec. The chamber exit air was passed through an XAD-4 vapor trap from which the pesticide was subsequently extracted and analyzed by the same methods as for field air. Volatilization flux was then calculated from the amount volatilized per interval of run time. The water remaining after each run was also analyzed for unvolatilized residue to achieve a mass balance. The total run times were approximately 1 day for thiobencarb and molinate, and 7 days for MCPA. Because of the longer run time in the latter case, distilled water was added at the end of each day to replenish that lost by evaporation.

To study volatilization from dry deposits of MCPA, 5 μg of either MCPA or MCPA-DMA were coated from a standard solution on round polyethylene caps (5.52 cm^2 area). The caps were allowed to remain at ambient conditions (24°C in the laboratory) in the open for 3 days. The amount volatilized was calculated as the difference between the initial and final amounts.

Field Flux Measurements

For MCPA, a 37 ha field consisting of 5 contiguous pads located in Glenn County, CA, was used. A 0.6 x 7.3 m wooden pier extended into the field from the midpoint of the west border (dike) of a central pad. The end of the pier supported two high volume air samplers, two rotating 3-cup anemometers (Met One Company), and two aluminum foil-shrouded thermometers. One item of each was positioned at 48 cm, and the other at 195 cm above the water surface. Humidity, vertical wind deflection, and wind direction were measured at the upper height. Background air samples were taken on 6-21-83, downwind air samples on 6-22-83 during the application (0.86 L/ha of Platte 48.6% MCPA-DMA diluted in water or 0.87 kg/ha a.i., applied by fixed wing aircraft) at 0615-0700, and flux samples at regular intervals of 2 hr each during daylight hours commencing on 6-22-83 and ending on 6-25-83. Water samples (composites of at least 10 grab samples) were taken from the pier area on the same schedule.

For thiobencarb, the same field used for MCPA was treated at 0915-0955 on 5-30-83 with 45 kg/ha of Bolero 10 G granules (4.5 kg/ha thiobencarb) by fixed wing aircraft. The sampling procedures were essentially as described for MCPA, on the dates 5-30-83 through 6-3-83.

For molinate, a 41 ha field located in the same vicinity as for MCPA and thiobencarb was divided into 14 paddies. A pier was constructed extending from the south edge of a central paddy into the field and again holding air sampling equipment essentially as described for MCPA and thiobencarb, except that low volume samplers were used. Background air samples were taken at 0730-0930 on 6-6-83, and downwind air samples during application at 1645-1845 on 6-6-83 (31 kg/ha of Ordram 10 G, or 3.1 kg/ha of molinate, by fixed wing aircraft). Flux samples were collected at 2 hr intervals during daylight hours starting at 1850-2045 on 6-6-83 and ending on 6-9-83. A prior application of molinate had been made to the same field on 6-1-83 (45 kg/ha of Ordram 10 G).

The aerodynamic method (9, 10) was used to calculate flux from air concentration and windspeed data. This will give an approximate flux because two measuring heights were used.

Preliminary Field Experiments (MCPA)

Three rice fields located approximately 6 km south-southwest of the city of Durham, Butte County, CA, were treated commercially one time each with MCPA-DMA. Air sampling was conducted inside the field and at field perimeters for MCPA and CLOC. The aerodynamic flux measurement was not made at these locations. All applications were made by fixed-wing aircraft. Field 1, 65 ha, was treated at 0600-0730 on June 17, 1979, with 1.03 kg/ha of Rhomene MCPA-DMA. The application at field 1 was not monitored, but air samples were taken at several distances extending to 1.9 km south of the field and adjacent to and inside an almond orchard north of the field for intervals up to 2 days after application. Samples were also taken above the treated field on days 1 and 2 after treatment. Field 2, 90 ha, was treated at 0817-0945 on June 22, 1979, with 0.84 kg/ha of Dow MCPA-DMA (MCPAmine). Air samples were taken at several downwind distances and inside an almond/walnut orchard and bean field located upwind during application, and at the same locations up to 3 days after application. Additional air samples were taken directly above the rice field at 1 and 3 days after application. Field 3, 250 ha, was treated at 1008-1150 on June 30, 1979, with 0.84 kg/ha of Dow MCPA-DMA. Air samples were

again taken at several downwind and upwind sites during application and at 0.5-1 hr after application. The wind direction and speed were recorded continuously by a nearby portable weather station.

Air Sampling and Analysis

High-volume air samplers (Sierra-MISCO, Staplex, or equivalent) capable of processing air at flow rates of ca $1 \text{ m}^3/\text{min}$ were fitted with 8.8 cm inside diameter aluminum sleeves at the air intake. A 100-mesh stainless steel screen in the bottom of each sleeve supported the sampling medium (100 ml of XAD-4). Low volume air sampling for molinate flux was done by adapting high-volume air samplers with a manifold which simultaneously pulled air at 40 to 60 L/min through each of 3 4 x 12 cm cartridges containing 60 mL of XAD-2 resin. In either case, the inlet side of the XAD chamber was left open to the air with no filter; it was positioned away from direct sunlight when in operation. After sampling was completed, the XAD resin was placed in screw-cap jars, and kept frozen (-10°C) until analyzed.

For MCPA, the resin sample was extracted with methanol (2 x 150 ml) on a rotary shaker for 2 hr, decanted and filtered. The combined filtrates were concentrated to 20 mL, diluted with 100 mL of 0.1 N H_2SO_4 containing 5% sodium sulfate and extracted with methylene chloride (3 x 40 mL). The combined extracts were concentrated to 1-2 mL and methylated with 4 mL of ethereal diazomethane at room temperature for 15 min. The methylated samples were dissolved in hexane for GC analysis. When further cleanup was required, the extracts were exchanged to benzene (5 mL) and eluted from a 7 x 1.6 cm Florisil column with 6% diethyl ether in benzene (40 mL) prior to GC analysis. Recoveries from XAD-4 spiked with 1-5 μg MCPA or MCPA-DMA and subjected to 2 hr air flow at $1 \text{ m}^3/\text{min}$ were >80%. For CLOC (1-5 μg) spiked as vapor to XAD-4 in an air sampler (2 hr, $1 \text{ m}^3/\text{min}$), the recoveries averaged 64%.

For thiobencarb and molinate, the XAD resin was extracted by sonication (30 min) with acetone (250 mL). The filtrate and 2 washings were concentrated to near dryness, and then taken up in hexane for GC analysis. Recoveries for 50 μg spiked to resin with no air flow were 95% (thiobencarb) and 80% (molinate). These compounds were trapped from spiked air with >70% (molinate) or 90% (thiobencarb) efficiency under air flows used in the field.

Water Analysis

For MCPA, each composite water sample (800 mL) was adjusted to pH 2 and extracted with methylene chloride (3 x 50 mL); the extracts were concentrated, 5 mL of methanol added, and subjected to methylation and GC analysis as described for the air samples. Recoveries averaged 74% for a 14 ppb fortification. For thiobencarb and molinate, each composite water sample (800 mL) was extracted with methylene chloride (3 x 50 mL), the extracts concentrated, and the volume adjusted for GC analysis. Recoveries were 95% for both compounds, with a detection limit of 5 ppb.

RESULTS AND DISCUSSION

Physical Properties

Volatilization from water is a first-order process which can be modeled using the two-film theory with Henry's Law constant (H) used to represent the interface equilibrium (11). The rate of volatilization for low volatility components is a direct function of H under constant environmental conditions. H was calculated for the compounds of interest using values of water solubility (S) or vapor pressure (P) obtained from the literature or experimentally determined (Table I). For thiobencarb, a major discrepancy was found in that our experimental P [obtained using the gas saturation technique (12, 13)] was 1.5×10^{-5} Torr at 20°C -- approximately 10 times greater than a commonly quoted literature value [1.476×10^{-6} Torr at 20° (14)]. Our re-examination of this value was prompted by poor initial agreement between EXAMS-predicted and chamber-measured flux values for thiobencarb.

Table I. Physical Properties of Compounds of Interest
(25°C unless otherwise specified)

	MW	MP	Water Solubility ^a	Vapor Pressure ^b	Henry's Law Constant ^c
MCPA (acid)	200.6	118-9	1,500	5.9×10^{-6d}	1.0×10^{-9}
MCPA (DMA salt)	244.7	--	>300,000	1.0×10^{-7}	$<10^{-13}$
4-Chloro-o-cresol	142.6	51	4,000	2.4×10^{-2d}	1.1×10^{-6}
Thiobencarb	257.8	--	30 (20°)	$1.5 \times 10^{-5}(20°)^d$	1.7×10^{-7}
Molinate	187.3	--	800 (20°)	3.1×10^{-3}	9.6×10^{-7}

^a in mg/L

^b in Torr

^c in $m^3 \cdot atm/mole$

^d Values measured in this laboratory. All other values are from literature sources.

Volatilization Rates -- Laboratory Chamber and EXAMS

A laboratory chamber described previously was used to measure volatilization rates from water (8). The measured flux values were normalized on initial water concentration to allow for comparisons among chemicals (Table II). Thiobencarb was also run once at a much lower initial water concentration (0.57 ppm) yielding a normalized flux in good agreement with that obtained at 16.3 ppm.

Table II. Volatilization Rate and Flux Measured in a Laboratory Chamber^a

Chemical	Concentration (ppm)		Run Time(hr)	Percent Mass Balance	Percent Volatilized	Volatilization Rate Constant (hr ⁻¹)	Normalized Flux (ng/cm ² ·hr·ppm)
	Initial	Final					
MCPA (pH 3.5)	99.8	90.2	153.5	82.9	0.015	9.78×10^{-7}	4.1×10^{-3}
Thiobencarb	16.3	14.8	22.8	94.9	12.2	0.00569	23.8
Molinate	25.1	18.9	22.7	97.4	28.6	0.0150	62.8

^a Results are averages of 2 runs (thiobencarb and molinate) or a single run (MCPA). Good agreement was obtained between duplicates.

EXAMS, a sophisticated computer model, uses physicochemical properties and environmental parameters as inputs to calculate dissipation rates for organic chemicals in water (5). While it was designed for dynamic water conditions in which the pollutant is added continuously to a flowing body of water, it can also be used for intermittent loadings to a static water body such as exists for waste evaporation ponds (6) and, in the present case, flooded rice fields. To obtain volatilization rate constants for comparison with the laboratory chamber, the dimensions (surface area and depth) of the chamber volatilization dish were used as input along with the water pH, wind speed, and temperature used in the chamber. While EXAMS would not accept the same chemical loads used in the chamber, this did not matter in the final comparisons because flux values were calculated from first-order rate constants which are independent of load. A pH of 3.5 was used for MCPA solutions in both EXAMS and laboratory chamber to ensure that a significant fraction (26%) of undissociated MCPA existed in solution for volatilization recognizing that the pKa for MCPA in water is 3.05 at 25°C (15). EXAMS-calculated flux values were 8.1×10^{-3} , 4.5, and 51.5 ng/cm²·hr·ppm for MCPA, thiobencarb, and molinate, respectively. These values agreed reasonably well with the laboratory chamber measurements (Table II), particularly considering that the range for the three compounds extended over 4 orders of magnitude. Sources of error for EXAMS-calculated values include the physicochemical property input, for which we relied on literature values of unknown accuracy (except for vapor pressures of MCPA and thiobencarb which were measured experimentally).

Volatilization Rates -- Field

In order to obtain environmental flux values for comparison with the laboratory-measured and EXAMS-calculated results, measurements were made during daylight above rice fields treated with MCPA, thiobencarb, or molinate during the 1983 growing season in the Sacramento Valley. A simplified version of the aerodynamic method (9, 10) was used, in which air concentrations and wind speeds were measured at just two heights (rather than the usual 4-6) above flooded fields for up to 4 days after treatment. Details of the method and tabulation of all results are in Ross et al (16). Only the daily averages from 3-5 sampling intervals each day are reported here (Table III). The trends in all 3 cases were for the highest normalized flux on the day of treatment, and then much lower values on days 1-3 showing a gradual decrease with time after treatment. The high day 0 values reflect non-equilibrium conditions on that day, with much airborne residue originating from chemical intercepted by pad dikes and perhaps

Table III. Average Daily Volatilization Flux Values From Commercial Rice Fields.

Chemical	Day After Treatment	Volatilization Flux (ng/cm ² ·hr)	Water Conc. (ppm)	Normalized Flux (σn) ng/cm ² ·hr·ppm
MCPA	0	4.37	0.26	16.8
	1	0.36	0.13	2.8
	2	0.25	0.18	1.4
	3	0.25	0.16	<u>1.6</u>
				\bar{x} (1-3) = 1.9 (0.8)
4-CLOC	0	1.27	0.0014	880
	1	0.43	0.0013	330
	2	0.27	0.0012	220
	3	0.24	0.0013	<u>180</u>
				\bar{x} (1-3) = 243 (78)
Thiobencarb	0	37.3	0.079	472
	1	7.9	0.35 ^a	23
	2	15.6	0.57	27
	3	5.6	0.57 ^a	<u>20</u>
				\bar{x} (1-3) = 23 (3)
Molinate	0	575	3.4	169
	1	193	2.9 ^a	66
	2	110	2.4	46
	3	58	2.1 ^a	<u>28</u>
				\bar{x} (1-3) = 47 (19)

^a Approximate values, interpolated from results for water for days 0, 2, 4, 6, and 8.

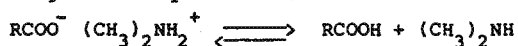
other surfaces, and general contamination of the air from drift during application. Furthermore, the dissolution of thiobencarb and, to a lesser extent, molinate from the applied granules was not complete on day zero, as was reflected in lower water concentrations on that day than on succeeding days (Table III). The higher water solubility of molinate (Table I) explains its higher concentrations in this medium, and perhaps the higher rate of dissolution when compared with thiobencarb even though both chemicals were applied as granules at similar rates. CLOC, a formulation impurity (~0.5%) and potential conversion product of MCPA (17), was measureably present in both water and air. While of peripheral interest here in that we addressed only the water to air distribution, it may be noted that the major residues of thiobencarb (50% or so of the total residue found) was associated with the sediment while for molinate the distribution favored the water phase (16). This distribution was not measured for MCPA but, from prior work (18), it may be assumed to also favor the water, particularly at the slightly alkaline field pH which would lead to virtually complete dissociation of MCPA.

The field-measured values using either day 1 or the average of days 1-3 agreed quite well with the laboratory-measured values for thiobencarb and molinate (Table IV), even though the

Table IV. Summary of Normalized Flux Values.

Chemical	H (atm·m ³ /mole)	Flux (ng/cm ² ·hr·ppm)			
		EXAMS	Laboratory Chamber	Rice Field Day 1	x Days 1-3
MCPA (acid)	1.0 x 10 ⁻⁹	8.1 x 10 ⁻³ (pH 3.5)	4.1 x 10 ⁻³ (pH 3.5)	2.8	1.9
MCPA-DMA (salt)	<10 ⁻¹³	0.0000	----		
4-Chloro-o-cresol	1.1 x 10 ⁻⁶	----	----	330	243
Thiobencarb	1.7 x 10 ⁻⁷	4.5	23.8	23	23
Molinate	9.6 x 10 ⁻⁷	51.5	62.8	66	47

environmental conditions were only approximately matched for the two measurements. The field-measured value also agreed quite well with the EXAMS-calculated value for molinate and, to a lesser extent, for thiobencarb; again, the environmental conditions were only approximately matched for field and EXAMS. For MCPA, however, field-measured flux was considerably higher than expected based on EXAMS and the laboratory chamber (Table IV), a finding further corroborated by measurements of significant residues of MCPA (up to 12 ng/m³) 400 m downwind from the treated field 1 hour after application ended. This may be explained as follows: Among the three herbicides, only MCPA was applied as an aqueous spray (as the DMA salt) when rice and weed foliage protruded above the water surface. As water evaporated from the deposits on field foliage, and on soil and foliage of the pad dikes, the MCPA-DMA salt released MCPA according to the equilibrium:



Evidence supporting this hypothesis was obtained from measurement of P using the gas saturation technique, which gave similar values for MCPA (12.70 x 10⁻⁶ Torr at 40°) and MCPA-DMA (2.73 x 10⁻⁶ Torr at 40°) coated on sand. Also, when MCPA or MCPA-DMA were applied to polyethylene surfaces and then left open to the air for 3 days at 24°, there was no difference between the volatilization rates of the two, as 90% volatilized (average volatilization rate, 0.27 µg/cm²/day) in each case. Finally, when a deposit of MCPA-DMA on sand was swept with nitrogen, over 60% of the dimethylamine in the salt was recovered in a downstream HCl trap during a 46 hr period. Thus, the higher than expected flux in the field treated with MCPA-DMA originated from equilibration between salt and free acid on dry surfaces followed by volatilization of MCPA. Because of this, the EXAMS-calculated and laboratory chamber-measured flux, which assumed only water as the contributing surface, did not simulate the conditions in the field. Release of MCPA from surface MCPA-DMA residues may also explain the presence of low concentrations of MCPA vapor observed in downwind air samples collected in neighboring fields and orchards well after spraying ended.

CLOC represents an interesting contrast to MCPA and MCPA-DMA with regard to volatility. Although at best only a trace component of the applied formulation, CLOC should volatilize rapidly from the deposited formulation in the environment. Furthermore, CLOC may form rapidly from MCPA in sunlight-irradiated water solution (18) or in irradiated deposits of MCPA-DMA (17) and should volatilize essentially as formed from water owing to its high H, and from surface deposits owing to its high P (Table I). In fact, air samples taken just above, and downwind from rice fields treated 1 or 2 days previously with MCPA-DMA showed generally more CLOC than MCPA. And air samples taken several kilometers from known application sites in the Sacramento Valley gave up to 30 ng/m^3 of CLOC -- roughly twice that of MCPA -- during the peak of the MCPA spraying season. Thus CLOC may represent the major MCPA-related air residue under environmental conditions.

CONCLUSIONS

Both the laboratory chamber and EXAMS computer model show good potential for predicting the volatilization flux of pesticides applied to flooded fields. EXAMS calculations agreed fairly well, and laboratory chamber measurements agreed very well with field results for thiobencarb and molinate. However, more chemicals must be studied, and more field measurements using more refined measurement techniques must be obtained before the results for these two pesticides can be considered generally representative for a range of chemicals and environmental conditions. For the present, either EXAMS or the laboratory chamber can be used as described here to obtain trends expected for volatility losses under field conditions, and as guides to indicate when full-scale field volatility studies are warranted. Furthermore, EXAMS affords the opportunity to vary environmental parameters (water depth, temperature, wind speed, etc.) to match those present in the field; while this capability was not investigated in this study, its application to environmental fate predictions is relatively straightforward.

For MCPA, neither EXAMS nor the laboratory chamber gave flux values approaching those observed in the field, but in this case the major sources of volatilized residue were deposits on dry foliage and soil surfaces rather than from solution in water. The MCPA case also showed the potential importance of a relatively minor contaminant/conversion product (4-chloro-o-cresol) having much higher volatility than the parent pesticide as a contributor to airborne residues.

Although our objective was to compare results from EXAMS, the laboratory chamber, and field in this preliminary evaluation, the findings do allow for assessment of the relative importance of volatilization as a fate process for the three herbicides studied. For molinate, Table III data yield a total volatilization loss of 1.1 kg/ha over a 4 day period following application, or 35% of the dose calculated to have been applied on day zero. For thiobencarb, the corresponding values are 0.07 kg/ha, or 1.6%, and for MCPA they are 0.006 kg/ha or 0.7% (not accounting for another 0.003 kg/ha lost as 4-chloro-o-cresol). Thus, it is only for molinate that volatilization is a significant route of loss of the total applied to a flooded field in this time interval, in keeping with prior estimates for this herbicide (19). It should be noted, however, that thiobencarb volatilization takes on more significance if only the applied dose dissolved in water is considered in this calculation. Using the

steady state water concentration of thiobencarb and its observed field volatilization rate (Table III), about 13% of the dissolved thiobencarb was calculated to have been lost to the atmosphere over a 4 day period. This is a somewhat lower rate than observed in prior commercial-scale field tests where $t_{1/2}$ for volatilization was on the order of 5-7 days (20). In making such comparisons, the important effects of temperature and wind must be considered as a major source of variability from one field test to another. Also, most estimates of percent lost by volatilization are based upon assumed application rates rather than the actual dose reaching the surfaces. The latter should be determined in order to accurately assess the relative importance of various fate processes.

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